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Progress Report, 1 June through 30 September 1961

INVESTIGATION OF THE EFFECT OF ULTRA RAPID QUENCHING  
ON METALLIC SYSTEMS, INCLUDING BERYLLIUM ALLOYS

Prepared for  
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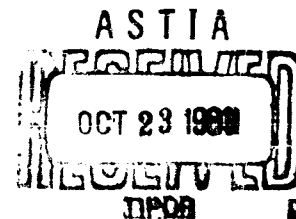
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#### ABSTRACT

This report summarizes the second four months progress of an investigation of the effect of ultra-rapid quenching on certain alloys of beryllium. The experimental techniques developed during the first four months were applied with only minor modifications to alloys of the systems Be-O, Be-Al, Be-Si, Be-Sc, Be-Ni, Be-Cu, and Be-Zn. No changes in phase appear to have been induced by ultra-rapid quenching in most of the alloys tested, although a shift of lattice parameter has been observed in several. Definite phase changes appear to have been induced in one Be-Cu alloy and in two Be-Ni alloys, but these results are subject to further confirmation.

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## 1 INTRODUCTION

This progress report covers the second four months work on the subject contract, namely the months of June, July, August, and September of 1961.

The general background and the development of the basic experimental techniques which have been used were fully described in EOS Report 1650-4M-1, and accordingly need not be repeated here. With the exception of some very minor changes, the apparatus and procedures have remained the same as described in the report mentioned. The changes have consisted of wrapping the output coil of the induction heater with glass fiber tape, and inserting a ceramic sleeve between this output coil and the graphite nozzle which it surrounds. The sleeve acts both as a shield to retard loss of heat from the nozzle and as a dielectric to prevent formation of an arc discharge between nozzle and coil; the glass tape serves to prevent arc formation between turns of the coil. Both these changes were made because of the problems encountered in melting and quenching alloys with relatively high melting points (say above 1300 C). Arc formation is encouraged both by the higher voltage being fed to the output coil and by the presence of an argon atmosphere (which requires an appreciably lower field for breakdown than, for example, air under standard conditions). Use of the tape and the sleeve have made possible satisfactory melting of all the alloys thus far investigated.

## 2 RESULTS

For the sake of clarity of presentation, the results obtained will be discussed in terms of each of the alloy systems investigated. Compositions will be given as weight percent beryllium present, using the common abbreviation "w/o Be". The systems will be discussed in order of increasing atomic number of the alloying element.

### 2.1 Beryllium-Oxygen System

Little information is available with respect to this system in either of the comprehensive collections which have become widely accepted as authoritative (Refs. 1 and 2). Moreover, the gaseous nature (under standard conditions) of one of the components makes control of the compositional variable difficult. The investigation of the Be-O system within the scope of the present program is therefore limited. The only technique available for attempting to get oxygen into solution in beryllium was to melt Be in contact with the intermediate phase BeO (whose existence, composition, and structure are well established). Since all of the alloys investigated in the entire program have been prepared by melting in BeO crucibles, any O transferred from BeO to solution in Be by contact melting should appear (as a shift in lattice parameter) in all alloys; thus no difference could be expected upon further attempts in this direction. Nevertheless, the experiment of melting Be in a BeO crucible with some particles of BeO (produced by crushing a short length of BeO tubing) was tried. As expected, no difference in the X-ray pattern of the resulting ingot could be detected. An alternative approach, suggested by the project monitor, was subsequently tried. The Brush Beryllium Co. supplies several grades of Be powder of varying oxygen content; it might therefore be



expected that these different grades would have different lattice parameters and provide source material for investigating the effect of ultra-rapid quenching. Accordingly, samples of each of the three grades of powder were obtained, and a specimen of each was melted and X-rayed. It was noted that each melt separated into two parts, one of which was roughly spherical in shape and had a bright metallic luster, and the other of which had a dark surface and an irregular shape. Each part was X-rayed separately. It was found that both parts of all three grades of Be showed the powder pattern of Be with no measurable variation in spacings from those of the pattern of Pechiney Be. In addition, the three darker portions showed several lines which coincided in spacing with the strongest lines of the pattern of BeO (as given on card 4-0843 of the ASIM file, Ref. 3). Moreover, the analysis furnished by the vendor gives the percentage (presumably by weight) of BeO present in each of the powders furnished, as follows:

| <u>Brush Designation</u> | <u>Percent BeO</u> |
|--------------------------|--------------------|
| SP-100                   | 0.89               |
| SP-200                   | 1.69               |
| SP-300                   | 2.09               |

The indications are, therefore, that the oxygen was present in the source material as BeO, rather than in solid solution in Be. If this is true, then of course there has been no gain in using the Brush powders, as the preparation procedure would still consist of melting Be in contact with BeO. However, it is planned that both portions of each grade of powder will be subjected to ultra-rapid quenching.

## 2.2 Beryllium-Aluminum System

According to Ref. 1, the elements Be and Al show no mutual solid solubility, but form a eutectic at about 1 w/o Be composition, with a melting point of 645 C. Samples of compositions 1, 5, and 80 w/o Be were prepared and quenched by the usual procedures (as described in EOS Report 1650-4M-1), except that it was found necessary to add a flux in order to induce mixing of the molten Be and Al; sodium fluosilicate ( $\text{Na}_2\text{SiF}_6$ ) was used for this purpose. Before quenching, only the lines due to Al were found in the X-ray patterns of the 1 and 5 w/o Be specimens, as was to be expected with such small concentrations of Be. The 80 w/o Be specimen showed the lines of both Be and Al in the pattern. After rapid quenching, no qualitative change was found in the structures; the 1 and 5 w/o Be samples still showed only Al, and the 80 w/o Be still showed only Be and Al. The parameter of the Al was not found to be measurably different from the ASTM value of  $4.0494 \text{ \AA}$  in any of these patterns except possibly those of the 5 w/o Be alloy, which were found to be  $4.047 \text{ \AA}$  before quenching and  $4.045 \text{ \AA}$  after quenching. However, it seems doubtful that these slight variations are significant, especially in view of the results obtained from the other alloys.

### 2.3 Beryllium-Silicon System

The Be-Si system is qualitatively similar in equilibrium properties to the Be-Al system, in that the two components show no mutual solid solubility but form a eutectic at a composition of 39 w/o Be with a melting point of 1090 C. Specimens having the compositions 20, 40, 60, 75, 80, and 90 w/o Be were prepared and quenched by the usual procedures. X-ray patterns made prior to quenching showed the samples to be mixtures of Be and Si, in agreement with the reported equilibrium properties (Ref. 1), except that only the strongest line of Be appeared in the 20 w/o Be specimen. After quenching, only a few Be lines appeared in the patterns of the 20, 40, 60, and 75 w/o Be specimens, so that no significant measurement of the lattice parameters could be made; in the 80 and 90 w/o Be specimens no change in spacings from those of the ASTM file could be detected. On the other hand, the Si reflections appeared clearly in the 20, 40, 60, and 75 w/o Be specimens, but only four Si reflections appeared in the patterns of the 80 and 90 w/o Be specimens. No other phases appeared after quenching. The parameter of the Si, as calculated from the (531) reflection, showed some variation in the four low-Be alloys (in which it could be measured\* with some accuracy) as follows:

| <u>w/o Be</u> | <u>Parameter (<math>\text{\AA}</math>)</u> |
|---------------|--|
| 0             | 5.4301 (ASTM value for Si)                 |
| 20            | 5.438                                      |
| 40            | 5.406                                      |
| 60            | 5.393                                      |
| 75            | 5.407                                      |

There is therefore some indication that some Be may be taken into solid solution in Si in the 40, 60, and 75 w/o alloys as a result

of rapid quenching, since the parameter of the Si appears to be lowered by an amount larger than could be ascribed to experimental error. However, it would seem that some lowering of the parameter should in that case also be observed in the 20 w/o Be alloy. This question will be further investigated.

#### 2 4 Beryllium-Scandium System

Investigation of this system is somewhat handicapped by the fact that neither Ref. 1 nor Ref. 2 gives any information about its equilibrium properties. It is therefore impossible to select logical compositions (such as those of intermediate phases or eutectics) for experimentation. In view of the technological interest in producing ductile Be alloys, the high-Be compositions 80 w/o Be and 90 w/o Be have been chosen as a starting point. It was found necessary to use a flux ( $\text{Na}_2\text{SiF}_6$ ) to induce the molten Be and Sc to combine. X-ray analysis of the resulting alloys show that at both compositions there is apparently an intermediate phase formed; the powder patterns are alike and consist of a very large number of lines. It is of course impossible to conclude that the complexity of the patterns is not due to the presence of more than one phase, either because the Be-Sc system really has a two-phase region at these compositions or because true equilibrium was not attained in the experiments. In any event, the alloys will be subjected to rapid quenching and again X-rayed to determine whether any change of structure has been produced.

## 2.5 Beryllium-Nickel System

This system consists of the intermediate phases BeNi and  $\text{Be}_{21}\text{Ni}_5$ , with eutectics formed between them and between the terminal solid solutions and the adjacent intermediate phase (Refs 1 and 2). These three eutectics and two intermediate phases were selected for investigation, the compositions being as follows:

| <u>Composition</u><br><u>(w/o Be)</u> | <u>Significance</u>                                   |
|---------------------------------------|---|
| 5.7                                   | Eutectic between Ni and BeNi                          |
| 14                                    | Intermediate phase BeNi                               |
| 25                                    | Eutectic between BeNi and $\text{Be}_{21}\text{Ni}_5$ |
| 40                                    | Intermediate phase $\text{Be}_{21}\text{Ni}_5$        |
| 58                                    | Eutectic between $\text{Be}_{21}\text{Ni}_5$ and Be   |

The alloys of this system were among the most difficult to prepare because of their relatively high melting points, but the apparatus changes mentioned earlier in the report (i.e., wrapping the output coil with glass fiber tape and using a ceramic sleeve around the graphite nozzle) made it possible to obtain satisfactory results. X-ray patterns of all five alloys prior to quenching showed them to consist of the correct equilibrium compositions as shown in the tabulation above. After rapid quenching, the patterns of the 5.7 and 14 w/o Be alloys were found to be the same as they had been before quenching. The remaining three alloys were changed as follows:

| <u>Composition</u><br><u>(w/o Be)</u> | <u>Pattern after Quenching</u>  |
|---------------------------------------|---|
| 25                                    | Strong BeNi plus unidentified lines<br>(not $\text{Be}_{21}\text{Ni}_5$ )   |
| 40                                    | BeNi only   |
| 58                                    | New phase tentatively analyzed as face-centered cubic with parameter 4.05 Å |

Since these results appear to represent complete changes of phase on quenching, it is important that they be checked carefully. Experiments designed to prove or disprove the authenticity of these results are now in progress. They consist of two approaches. first, repetition of the preparation and quenching to determine whether the same results can be obtained, and second, heat treatment of the quenched samples to determine whether reversion to the equilibrium structure can be induced. Reversion to equilibrium would be conclusive proof that a true change in structure had been produced by quenching, and that the observed changes in X-ray diffraction patterns were not due merely to an accidental alteration of composition, for example. The quenched 40 w/o Be alloy has been heated 12 hours at 200 C and 1 hour at 400 C without causing a reversion of the BeNi pattern to the equilibrium phase  $\text{Be}_{21}\text{Ni}_{15}$ .

It is of interest to note the variation in the lattice parameter of the BeNi phase obtained by several different procedures

| <u>Specimen</u>         | <u>Parameter (<math>\text{\AA}</math>)</u> |
|-------------------------|--|
| 14 w/o Be before quench | 2.601                                      |
| 14 w/o Be after quench  | 2.613                                      |
| 40 w/o Be after quench  | 2.616                                      |

The parameters were calculated by averaging the values obtained from 5 high-angle reflections of each pattern. For comparison, Ref. 1 states that the parameter of BeNi varies from  $2.62\text{\AA}$  at 13.4 w/o Be to  $2.61\text{\AA}$  at 14.5 w/o Be.

## 2.6 Beryllium-Copper System

According to Ref. 1, the Be-Cu system consists of terminal solid solutions and three intermediate phases designated  $\beta$ ,  $\beta'$  and  $\gamma$  in order of increasing Be content. The  $\beta$ -phase is centered about the composition 6 w/o Be (roughly  $\text{BeCu}_2$ ), the  $\beta'$ -phase about 12 w/o Be (roughly  $\text{BeCu}$ ), and the  $\gamma$ -phase about 30 w/o Be (roughly  $\text{Be}_3\text{Cu}$ ). Since all three phases exist over a range of composition (although the range is narrow in the case of the  $\beta'$ -phase) it is probably preferable to use the Greek-letter designations. The compositions selected for investigation corresponded to these three intermediate phases, plus two high-Be alloys (80 w/o and 90 w/o Be) included because of the technological interest in obtaining ductile Be. Both the 80 w/o Be and the 90 w/o Be compositions lie in the Be-rich terminal solid solution (Ref. 1).

All the alloys were prepared and quenched by the usual procedures. X-ray patterns made prior to rapid quenching showed that the alloys had the correct equilibrium structures, except that poor patterns were obtained from the  $\beta$  and  $\beta'$  phases. However, after quenching, these alloys yielded clear patterns of (respectively) the  $\beta$  and  $\beta'$  phases only, indicating that the compositions were correct as prepared, and that the unsatisfactory patterns were probably due to incomplete alloying. With the exception of the 30 w/o Be alloy ( $\gamma$ -phase in equilibrium), none of the specimens showed any change of structure after quenching. The 30 w/o Be, which had yielded a clear  $\gamma$ -phase pattern before quenching, gave only a clear  $\beta'$ -phase pattern after quenching. In order to check this result, a new sample was prepared and quenched; again only a clear  $\gamma$ -phase pattern was obtained before quenching, but after quenching a weak  $\gamma$ -phase pattern appeared together with the strong  $\beta'$ -phase pattern. The tentative conclusion is that there is a transformation from  $\gamma$  to  $\beta'$  induced by quenching, and that in the second sample the quench was not quite as effective as in the first. Again, further work will be necessary to prove or disprove the point.



## 2.7 Beryllium-Zinc System

Very little information on the Be-Zn system is given in Refs. 1 and 2. It seems probable that little investigation of the system has been made because of the experimental difficulties encountered in attempting to alloy the two elements, since the boiling point of Zn (namely 906°C) is considerably below the melting point (1280°C) of Be. An attempt was made to form an alloy of Be and Zn in the present program, but the Zn evaporated and deposited in a film on the adjacent apparatus before the Be was melted. Consequently, it does not seem feasible to investigate the Be-Zn system within the scope of the present program, as the entire quenching apparatus would have to be rebuilt so as to operate in a high-pressure atmosphere.

### 3 FUTURE WORK

It is planned that the program will be continued along the following three lines

- 1 Using present techniques, extend work to include other alloy systems, or other compositions within the systems already investigated, which may be of interest

- 2 Using present techniques, attempt to conclusively settle any questions which have been left undecided at the present stage of the program. This point would consist largely of proving or disproving the authenticity of the phase transformations which have been found to be produced by rapid quenching

- 3 Adoption of a new improved design of quenching apparatus now being developed by Dawez and co-workers at the California Institute of Technology. It appears that the new design will be simple and inexpensive to construct, and should be checked out in the fairly near future. Since it is still in an experimental stage, description of it will be deferred to a future progress report

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1. M. Hansen, "Constitution of Binary Alloys", McGraw-Hill, 1958.
2. W. B. Pearson, "A Handbook of Lattice Spacings and Structures of Metals and Alloys", Pergamon Press, 1958.
3. "X-Ray Powder Data File", Sets 1-5, Inorganic, Amer. Soc. for Testing Materials, 1960.

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